SPARK PLASMA SINTERING THE SPARK-EROSION POWDERS OF FUNCTIONAL ALLOYS

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ABSTRACT

Various shape memory alloys (Ti-Ni-Hf, Ni-Al and Cu-Al-Ni) were elaborated by spark plasma sintering method from the micron, submicron and nano- sized particles prepared by spark-erosion method in cryogenic liquid from preliminary melted master alloys. These alloys are being developed as one of the alternatives for the intermediate temperature applications (100-900°C). Spark plasma sintering method is express method, which provides lower temperature and shorter holding time of sintering. It makes possible to sinter materials from the pre-alloyed powders and eliminate the intensive grains growth and precipitating processes influencing the mechanical and functional properties of functional materials. The effects of processing parameters on the martensitic transformation and microstructure of the sintered compacts were investigated using XRD and SEM study. Temperatures of sintering were chosen according to the assessed data of the decomposition, oxidation and others processes carrying out in material. Although the precipitating processes were usually not completely depressed, the intensive grain growth was also not found in most cases. Most of the microstructure peculiarities of as processed powder were inherited by the sintered material.

Key words: shape memory alloys, spark-erosion powders, spark plasma sintering, Ti-Ni, Ni-Al, Cu-Al-Ni

INTRODUCTION

Attractive perspectives for the practical application of modern functional materials such as materials with conventional and magnetic shape memory, high-temperature shape memory materials and bulk amorphous materials stimulate continuous searching of new production and processing methods, like powder metallurgy (PM). Search direction is caused by their typical characteristics and requirements that are imposed to them. In most cases shape memory materials (Ti-Ni-X, Ni-Al-X, Ni-Mn-Ga, Cu-Al-Ni-X) have precision composition. High temperature shape memory materials, moreover, contain or highly reactive components (Zr-Cu-X, Hf-Pd, Zr-Pd, Ti-Ni-Hf, Ti-Ni-Zr), or high-cost

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(Hf-Pd, Zr-Pd, Ru-Nb, Ru-Ta, Ti-Pt, Ti-Pd, Ti-Au). Bulk amorphous materials that act as precursors for the manufacture of shape memory materials (Ti-Zr-Hf-Ni-Cu) are a multicomponent. Most of the above mentioned materials tend to the decomposition during the heat treatment. In addition, they, with few exceptions, have poor ductility and machinability.

In this communication we will focus on three materials, which are representative most of above mentioned peculiarities of functional materials: Ti-Ni-Hf, Ni-Al and Cu-Al-Ni-Ti-Cr shape memory alloys (SMA). These kinds of SMA are being developed as ones of the alternatives for the intermediate and high temperature applications depending on the alloying content.

Enriched with Ni intermetallic Ni-Al is a promising shape memory alloy (SMA) for high-temperature applications. The start temperature of martensitic transformation varies from 200 to 1200K in the range of 60-70 at.% Ni. Currently, its wide application is limited by low plasticity, in particular due to the formation of intermetallic compounds Ni_3Al and Ni_5Al_3 during the preparation or heat treatment. By means of the traditional methods of the production (induction or arc melting) or by the sintering of elemental powders the obtaining of homogeneous alloys, free of these phases, is not achievable.

Cu-Al-Ni is considered as good candidate for the intermediate temperature applications (100-300°C). In Cu–Al–Ni, during the quenching the metastable β phase undergoes several types of martensitic transformation (MT) depending on Al content. The characteristics of the martensitic transformation MT are very sensitive to the order degree of the βphase and the precipitation processes. Primary $γ_1$ precipitation limits the high temperature applications of these alloys modifying the MT. The eutectic decomposition takes place above 440°C and finally the β→α+$γ_1$ eutectoid decomposition appears at 500°C. Increasing Al content promotes the formation $γ_1$ phase that embrittles the alloy. In addition Cu–Al–Ni alloys are brittle due to their very high elastic anisotropy (A~13) and large grain size and in general show poor mechanical properties. Powder metallurgy is to be a good method in order to obtain fine grain size in Cu–Al–Ni SMA.

Ti-Ni-Hf(Zr) alloys could perform reversible martensitic transformation at 100-150°C higher than the room temperature depending on Hf content. Although the decomposition processes modifying their properties were not found in the working interval temperature, the limited ductility, poor machinability and formability restrict theirs wide practical applications. As well as for Cu-Al-Ni, the powder metallurgy (PM) is thought to be good alternative method for their production and allowing skip over the stages of the shaping parts. Usually PM processes using for the production Ni-Ti-based alloys from elemental components impacts with unresolved synthesis problems: extra phases such as Ti_2Ni, Ni_4Ti_3, Ni_3Ti [1], contaminations like $Ti_4Ni_2O_x$[2]. Therefore the using of pre-alloyed powders looks as preferable way for PM processing.

In current work the spark erosion (SE) powders of Ti-Ni-Hf, Ni-Al and Cu-Al-Ni-Ti-Cr obtained in liquid argon were used [1,3,4,5]. Spark erosion is probably the most versatile technique available for producing the particles of metals, alloys, compounds with the diameters of particles from a few nm to >100 μm. In case of liquid argon used as working liquid, SE method allows obtaining the powders from pre-alloyed material with a given composition, which is vitally important for functional material like SMA, free from large quantities of oxides.

In turn, the operation with pre-alloyed powders has unambiguous feed-back caused by the peculiarities of the mechanism of powder sintering. The combustion sintering passing through the eutectic reactions or consumption the heat of formation of intermetallic compounds, promoting the sintering of ele-mental powders, is not available anymore. The mechanism of solid state diffu-sion sintering between the different powders particles of the same composition presumes the long term ageing. The precipitation processes are superimposed on the sintering processes during the annealing causing a decomposition of alloys with the formation of supplementary phases. Therefore the spark plasma sintering (SPS) method looks as a promising alternative of the conventional sintering method of pre-alloyed powders.

SPS method is express method allowing the sintering powders within 10 minutes in vacuum or inert gas atmosphere. It employs simultaneously the relatively high pressure, high temperature of sintering and heavy current pass-ing through the samples that destroys the oxidation film on the powder surface providing good sintering. The method is very informative. It gives "on line" the information about the progress of the compacting, temperature interval of de-gassing and softening of the materials, which could be exceptionally useful for the optimization of the sintering regimes.

The goal of this work was to preliminary study the applicability of SPS method for the rapid sintering of pre-alloyed SE powders of Ti-Ni-Hf, Ni-Al and Cu-Al-Ni-Ti-Cr shape memory alloys.

EXPERIMENTAL PROCEDURE AND ANALYSIS

Commercially pure Ti, Ni, Cu and Hf and Zr (99.9%) were used for the al-loys production by the induction melting. The rods of Ni49.87-Ti40.25-Hf9.44-Zr0.30-Cu0.14at.% and Cu-13.01Al-3.91Ni-0.37Ti-0.24Crwt.% with a diameter of 6 mm was produced by AMT (Belgium). Alloy with a nominal composition $Ni_{63}Al_{37}$ arc melted and molded into bars with a diameter of 4 mm and the length of 12 cm. Part of the rods were used as electrodes for SE appa-ratus and the remaining were broken at 3-4 mm pieces and were used to obtain powder by spark erosion method.

The general principle of the spark-erosion processing was described in de-tails in [3,6] and involves the application of a heavy current between two elec-

trodes and a lot of pieces (chunks) that prepared from the pre-alloyed material both being immersed in a dielectric refrigerant inside a container. The key idea of the method is the melting (evaporation) of the material by the electric discharge with a duration of 5-100 μsec with subsequent quenching of molten droplets in liquid argon *in situ*. After spark erosion treatment of 100 g of granules of master alloys in liquid argon about between 40 to 70 g of powder was received depending on the material composition. In order to prevent eventual explosion of finest particles of powders it was kept in a vessel with liquid argon during the day until all argon was evaporated. Then the powders were sieved and divided into three fractions: the size of less than 128 and more than 65 μm, less than 65 and more than 32 μm and less than 32 μm.

Fig. 1 shows the main components of the SPS apparatus (DR.SINTER® LAB Series, Metal Processing Systems, Inc. Japan). A 50 kN uniaxial press together with an AC power supply simultaneously provide a mechanical load through the die plungers for densification and an alternating current through the sample placed in the graphite die. About 1 g of powder was preliminary slightly compacted in the die. A graphite paper was put between the sample and the graphite plungers. The die was then placed inside the working chamber of the apparatus and the system was evacuated. To avoid overheating of the sample the heating rate was no more 350 °C/min.
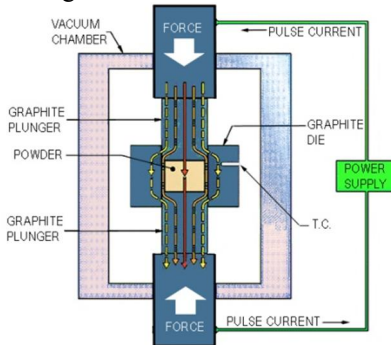

Fig. 1 A general scheme of spark plasma sintering apparatus

Maximum applied uniaxial pressure was 99.5 MPa. Temperatures of the samples during the sintering were measured by a sheathed thermocouple, which was inserted into a small hole in one side of the graphite mold, as illustrated on *Fig. 1*. The temperature, vacuum in the chamber, current applied force, shrinkage displacements of the powder compacts, voltage and current were recorded during the processing.

The electric current provides a rapid Joule heating in the compact die-sample system. The experiment is initiated with the heating by the application of continuously increasing electric current together with the continuously increasing pressure. When the temperature get to preliminary setting temperature of sintering (T_{SINT}) a set constant value of the electric current was applied for a given time, hereafter indicated as sintering time (t_S). After that, the sample was unloaded, cooled and removed from the die. Temperatures of sintering were chosen according to the assessed data of the decomposition, oxidation and others processes carrying out in material. A typical program of the sintering is shown

on *Fig. 2a.* The performed programs of sintering are listed in *Table 1*. As a result
of sintering a sintered compacts with a diameter of 8 mm and height of 4-6 mm
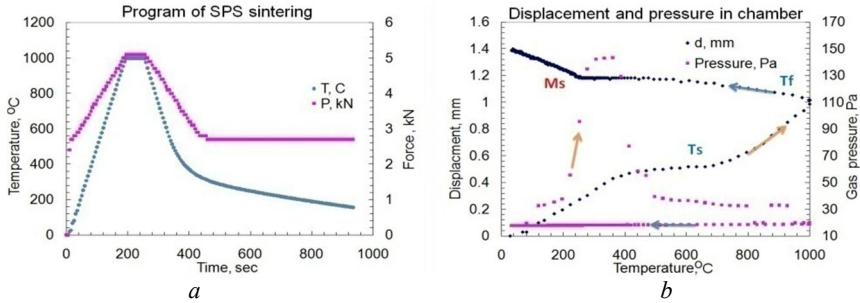were obtained.

Fig. 2 *a*) – typical program of sintering (T_S=1000°C; t_S=1 min); *b*) – shrinkage dis-
placement of the sample and gas pressure in the chamber vs. temperature

Table 1 – The regimes of SPS treatment; F – applied force, HR – heating rate,
D – displacement (shrinking)

Regime	T_{SINT}, °C	t_S, min	F, kN	HR, °C/min	D, mm	Remark
Cu-Al-Ni						
CAN-1000-1	1000	1		330	1.60	Melt, 32/65
CAN-700-1	700	1		280	1.97	MT, 32/65
CAN-650-1	650	1		160	1.72	MT, 32/65
CAN-600-1	600	1	5	150	1.72	MT, 32/65
CAN-480-1	480	1		96	1.52	32/65
CAN-440-1	440	1		88	1.07	32/65
CAN-390-1	390	1		65	1.05	MT?, 32/65
Ni-Al						
NA-400-10	400	10		200	0.22	32/65
NA-500-10	500	10		250	0.24	32/65
NA-850-10	850	10		212	0.87	MT, 32/65
NA-850-4s	850	4.5	5	212	0.86	MT, 32/65
NA-900-2	900	2		225	0.92	MT, 32/65
NA-850-4b	850	4.5		212	1.40	MT, 65/128
NA-1000-1	1000	1		250	1.53	MT, 65/128
Ti-Ni-Hf						
TNH-500-0	530	0	2.5	100	0.29	<32
TNH-1000-2	980	2		100	1.20	<32
TNH-860-1H	860	1	5	250	1.19	MT, 32/65
TNH-1000-1H	1000	1		200	1.42	MT, 32/65

XRD study of the compacts were carried out at room temperature by the Debye-Sherrer method with a $CoK\alpha_{1,2}$ radiation. Instrument Philips PW1830 with Multi-Purpose XRD Diffraction System from PANalytical were used.

The morphology and microstructure of the sintered samples were analyzed by LEO 1530 instrument equipped by PGT PRISM 2000 (Ge) spectrometer without the references standards. Detail composition study were carried out with JSM-6490LV(Jeol) and JAMP-9500F (Jeol) both equipped with EDX spectrometer INCA PentaFETx3 (Oxford Instruments).

RESULTS AND DISCUSSION

Fig. *2b* illustrates the behavior of the shrinkage displacement of the powder compacts and gas pressure in the chamber during processing. This behavior corresponds to the program of sintering NA-1000-1. The first stage of the sample shrinking is accompanied by the vacuum fall and connected with the mechanical compressing of powder and partial welding while the second one starts at about 700°C (T_S on figure) – with the sintering of the particles. Such a kind of behavior is typical for all powders. The temperature of the first (T_1) and second (T_S) shrinkage displacement upon the heating depends on the kind of powder. In case of Ti-Ni-Hf powder there was third interval too. Temperature intervals of sintering are listed in Table 2. First sintering interval contributes about 15%, 30-40% and 8-15% of the total displacement for Cu-Al-Ni, Ni-Al and Ti-Ni-Hf powders respectively. The value of contribution depends on the sizes of powders particles. The more the diameters of particle sizes, the more this contribution. Because the effect of preliminary compacting (before the processing) is the less, the more the particles size, this first interval can associate mainly with the initial mechanical shrinkage of the powders particles. It accompanied by the emission of gas (air), which is kept between the particles. The other process such as reverse martensitic transformation and precipitation of extra phases (Ni_5Al_3 in case of Ni-Al powders) can also contribute the shrinkage effect. It is seen also from Table 1 that the more the diameters of particle sizes (denoted in field "Remark" of *Table 2* like 32/65 – min and max sizes of particles in powder fraction), the more total shrinkage of the compact. Thus the succeeding sintering interval doesn't practically depends on the particles size and defined only by the high temperature plasticity of the material as well as the decomposition processes, which take place at this temperatures.

Table 2 – Temperature intervals of sintering

Powder	$T_{1\ start}$, °C	$T_{1\ finish}$, °C	$T_{S\ start}$, °C	$T_{S\ finish}$, °C	$T_{3\ start}$, °C	$T_{3\ finish}$, °C
Cu-Al-Ni	120	250	300	>700	-	-
Ni-Al	50	400	600-650	>1000	-	-
Ti-Ni-Hf	300	425	475	850	910	>1000

It is interesting also that upon the cooling the extra shrinkage appeared which was displaying as sharp incline on the reduction displacement curve (Ms on Fig. 2*a*, MT in Table 1). Because the position of sharp incline correlate with the martensitic start point of the respective powder on can assume that this extra compacting relates with the martensitic transformation stimulated by the external uniaxial pressure of the plungers.

The powders, which were sintered at relatively low temperature (<400°C), were mechanically stable (although special mechanical test were not carried out). However the best quality of samples was found for the compacts sintered at higher temperature within the interval 850-1000°C depending on the composition of powder.

SEM investigation confirmed that after the first stage of sintering only initial welding and partial compacting appeared. The particles remained mainly non-deformed with the typical round shape of SE powders (*Fig. 3*). Contrary, the particles after the second stage of sintering were gathered tight and have been deformed. EDS microanalysis has shown it is not possible avoid the decomposition processes during SPS processing even if the very short time of sintering was used. Typical for each of powders under investigation extra phases were found. The type of precipitates depends on the temperature of sintering mainly. γ_1 or α-phase or both of them were found in the compacts of Cu-Al-Ni after different sintering programs (*Fig. 4*). Enriched with Ni phase (perhaps Ni_3Al) was found in Ni-Al powder after NA-850-4s program (*Fig. 5a*). It seems to be inherited from the initial microstructure on Ni-Al SE powders described elsewhere [5]. It is interesting that after NA-1000-1program the traces of Ni_3Al phase were not found and some of the particles were recrystallized (*Fig. 5b*). Taking into account that this phase disappears after the heating above about 1150°C, also the fact that Cu-Al-Ni powder after heating to 900°C was melted, one can conclude that real temperature of the compact inside the die was high than the recorder one on about 150-200°C.
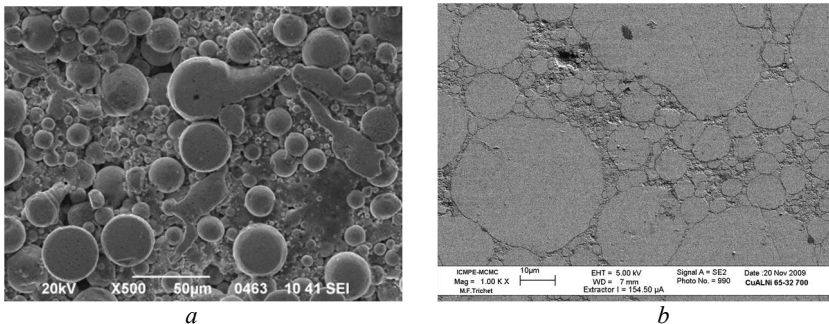

| a | b |

Fig. 3 – SE images of Cu-Al-Ni powder after the compacting programs *a*) – CAN-390-1, *b*) – CAN-700-1
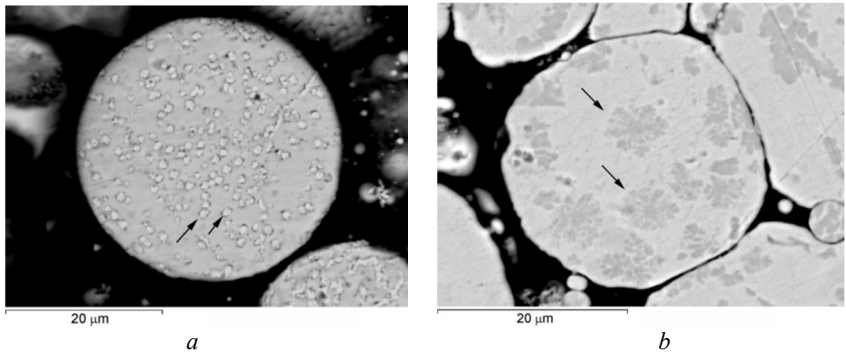
Fig. 4 – BSE images of Cu-Al-Ni powder after the compacting programs: *a*) – CAN-390-1, arrows show α-phase precipitates; *b*) – CAN-650-1 arrows show γ₁-phase precipitates
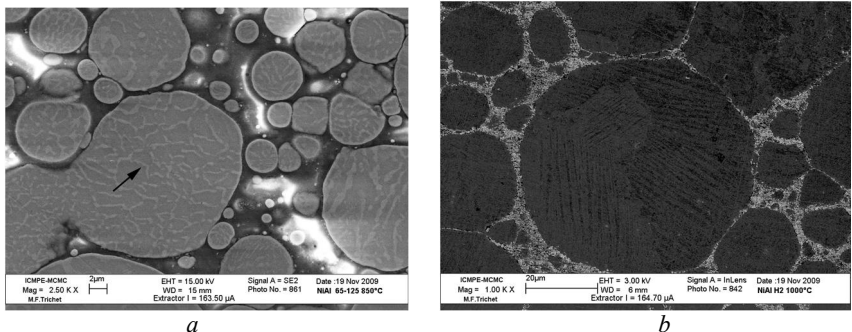

Fig. 5 – Ni-Al powder after the compacting programs: *a*) – NA-850-4s, arrows show the enriched with Ni precipitates; *b*) – NA-1000-1

Banded structure resembling the martensite was also found. In addition to the enriched with Ni phase (seems to be Ti₂Ni), a lot of enriched with Hf and oxygen precipitates (with the composition close to HfO₂) were found into Ti-Ni-Hf powders particles as well as on their boundaries (*Fig. 6*).

XRD study confirmed the results of SEM investigation. B2, 2H, 18R, γ₁ and α-phase or both of them are the main phases in the Cu-Al-Ni blends. In addition some noticeable quantity of Cu₂O was found.

Although the sintering time was rather short (1-4 min) it does not prevent the formation of the Ni₅Al₃ phase below 900°C; Ni₃Al phase has formed in the samples sintered at higher temperatures while the lowest amount of this phase was found for Ni-Al powders treated according to the program NA-1000-1. Some minute peaks could be considered as belonging to Al₂O₃ phase.
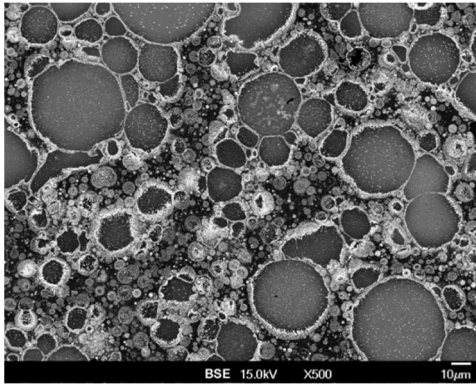
Fig. 6 – Ti-Ni-Hf powder after the compacting programs TNH-1000-1H. Bright spots are the enriched with Hf and oxygen phase

In addition to B2, Ti_2Ni and B19' (martensite) phases a lot of HfO_2 were found in Ti-Ni-Hf blends. The formation of the oxides in the sintered samples is due to pure vacuum and remains of the air, which is kept along with the preliminary compacted particles. The nano-fraction of powders, filling the interspaces between the micron sized particles, promotes also the oxidation; thus the oxides appear mainly between micron sized particles. One exception is Ti-Ni-Hf powder where chemically active Hf is oxidized in the middle of particles.

CONCLUSIONS

The powders of shape memory alloys with the compositions Ni49.87-Ti40.25-Hf9.44-Zr0.30-Cu0.14at.%, Cu-13.01Al-3.91Ni-0.37Ti-0.24Crwt.% and $Ni_{63}Al_{37}$ were elaborated by the spark plasma sintering method from the micron, submicron and nano- sized particles prepared by spark-erosion method in liquid argon from preliminary melted master alloys.

Although the powders were sintered already at relatively low temperature (<400°C), the best quality of samples was found for the compacts sintered at higher temperature within the interval 850-1000°C depending on the composition of powder.

Even the sintering time was rather short (1-10 min) it does not prevent the formation of extra phases. Most of the microstructure peculiarities of as-processed powder were inherited by the sintered material. The intensive grain growth was not found in most cases.

The remains of the air, which is kept in the interspaces between the preliminary compacted particles as well as nano-fraction of powders promotes the oxidation processes during the SPS processing.

The martensitic transformation in most of the sintered compacts has been clearly indicated during the cooling in spark-plasma apparatus; martensitic structure was confirmed by SEM and XRD study.

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